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Hisashi Hayashi, Noboru Watanabe and Yasuo Udagawa
Research Institute for Scientific Measurements
Tohoku University
Sendai 980-8577

Hisashi Hayashi and Chi-Chang Kao
National Synchrotron Light Source
Brookhaven National Laboratory,
Upton, NY 11973-5000

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Momentum dependence of $\pi - \pi^*$ excitations of benzene rings in condensed phases

Hisashi Hayashi^{a,b,*}, Noboru Watanabe^a, Yasuo Udagawa^a, Chi-Chang Kao^b

^a *Research Institute for Scientific Measurements, Tohoku University, Sendai 980-8577, Japan*

^b *National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY 11973, USA*

Abstract

Inelastic x-ray scattering (IXS) spectra for the $\pi - \pi^*$ excitation of benzene, toluene, polystyrene, and benzene-hexane solutions have been measured at medium momentum transfers (q), $0.35 \leq q \leq 1.5 \text{ \AA}^{-1}$. IXS profiles of these substances closely resemble each other. The $\pi - \pi^*$ peak of the pure substances shows a negative q -dispersion ($\sim 0.5 \text{ eV}$), while diluted benzene does not. For benzene, the loss function and the real (ϵ_1) as well as the imaginary (ϵ_2) parts of the dielectric function were deduced. It is shown that the $\pi - \pi^*$ excitation in liquids is well-localized and the q -dispersion can be interpreted by changes of the shielding factor $\epsilon_1^2 + \epsilon_2^2$. The properties of the loss function for molecular condensates are discussed.

Keywords: Inelastic x-ray scattering; Loss function; Medium momentum transfer; Molecular liquids; $\pi - \pi^*$ excitation; Condensation effects.

*Corresponding author. Tel. No.: 631-344-8033; Fax No.: 631-344-3238; e-mail address: hayashi@bnlls1.nsls.bnl.gov

1. Introduction

The action of radiation on molecular liquids is of crucial importance in many fields, e.g., radiation chemistry and radiation biology [1]. In principle, the interaction between radiation and matter can be fully described by the so-called loss function. The loss function is simply the imaginary part of the inverse dielectric function, $\text{Im}(-1/\epsilon(q, E))$ [2,3], and can be measured directly from inelastic scattering where the momentum q and energy E are transferred. The measurement of the loss function over a complete q - E range provides an indispensable basis for studies of radiation interaction in matter.

Unfortunately, knowledge of the loss functions for molecular liquids is quite insufficient, except near two 'extremes' in q . At the low/high q -limit, the loss function gives optical-absorption ($q \sim 0$) /Compton-scattering profile ($q \gg 1 \text{ \AA}^{-1}$) [3]. For molecular liquids, optical absorption spectra below $\sim 7 \text{ eV}$ [4] and Compton profiles [5] have been thoroughly investigated. On the other hand, loss functions for a large area in q - E space, especially for $q \sim 1 \text{ \AA}^{-1}$ and over a wide range of E at $q \sim 0$ have not been explored until recently, because of the lack of appropriate experimental tools.

With the developments of synchrotron radiation sources, however, it is now possible to apply inelastic x-ray scattering (IXS) to determine the loss functions of molecular liquids for $q < \sim 1 \text{ \AA}^{-1}$. Recently, by using IXS, we have measured the loss functions of several liquids for excitations to continuum states at various q 's [6-9]. In particular, we have measured the equivalent of an absorption spectrum for liquid water with IXS [6,7]. In this work, we have investigated the loss functions of benzene and related compounds for excitations to discrete states at $q \sim 1 \text{ \AA}^{-1}$. Specifically, the q -dependence of the $\pi - \pi^*$ excitation of benzene rings, located at $\sim 7 \text{ eV}$, is examined because it forms a well-defined peak in the absorption spectra [10,11].

2. Experimental

IXS spectra of liquid benzene, liquid toluene, solid polystyrene, and benzene-hexane solutions (25 and 50 mol% benzene) were measured at the wiggler beam line X21 of the National Synchrotron Light Source. Monochromatic x-rays, with 0.2 eV resolution, were used to irradiate the sample. X-rays scattered at an angle θ were collected and

dispersed with a spherically bent crystal analyzer (Si(444), 1m in radius) and detected with an AMPTEC XR-100T detector. For high/low resolution measurements, a Bragg angle of $87.5/79.7^\circ$ was employed. The corresponding pass energy of the analyzer was 7918/8038 eV. The energy resolution, measured as the FWHM of the elastic line, was 0.5/1.3 eV. Measurements were carried out in high resolution mode for $E \leq 10$ eV to resolve the $\pi - \pi^*$ peak in the spectrum, while the low-resolution mode was employed to achieve high S/N ratio for $E > 10$ eV. By varying θ from 5 to 21.5° , the q range $0.35 \leq q \leq 1.5 \text{ \AA}^{-1}$ was covered. The measured spectra were analyzed in a similar manner to that described previously [8,9].

3. Results and Discussion

3-1 IXS spectra for $\pi - \pi^*$ excitation region of benzene rings in condensed phases.

Figs.1 (a)-(d) show high-resolution IXS spectra, which are proportional to $q^2 \times \text{Im}(-1/\epsilon)$, in the $\pi - \pi^*$ region for benzene, toluene, polystyrene, and 25 mol% benzene-hexane solution. The overall spectral shapes for the four samples are similar, which suggests that the $\pi - \pi^*$ excitations are well localized at each benzene ring, and that the influence of the alkyl substituent and the bond formation connecting the rings is small.

A close look at the peak energies tells us that, although the $\pi - \pi^*$ peak energies in Figs.1 (a)-(c) are constant below $q=0.5 \text{ \AA}^{-1}$, the peak shifts by about 0.5 eV to lower E as q increases from 0.6 to 1 \AA^{-1} . Such negative dispersion has not been observed in molecular gases [12,13], and hence must be due to condensation effects. Interestingly, the negative dispersion is found to depend on the concentration of benzene; as the concentration decreases, the dispersion also decreases and in the lowest concentration studied, 25 mol% solution shown in Fig.1 (d), almost no dispersion is observed. The interpretation of these results will be given below, in section 3-3.

3-2 The loss function and the dielectric function of liquid benzene.

For liquid benzene, the loss function was deduced on an absolute scale, by the normalization [8,9] of IXS spectra up to 160 eV, and is shown in Fig. 2. The loss functions have two prominent features: a sharp peak located at ~ 7 eV and a broad maximum at around 20-30 eV. The former is well known to be due to the discrete $\pi - \pi^*$ excitation, and the latter to continuum excitations. Both peaks converge as q

decreases, and the spectra for 0.35 and 0.53 Å⁻¹ overlap within experimental error. This means that the dipole approximation for excitations in benzene is justified for $q \lesssim 0.5$ Å⁻¹ [7].

For $q > 0.7$ Å⁻¹, the loss function shows a clear q -dependence. With increasing q , the maximum broadens and shifts to higher E . At the same time, the intensity of the $\pi - \pi^*$ band is reduced. This is because higher-energy dipole forbidden excitations always occur at large q , and the integral of the loss function multiplied by E must be constant, from the sum rule [2,3]. For sufficiently high q (> 5.2 Å⁻¹), IXS can be considered to be Compton scattering and the spectra can be reproduced in terms of the reported Compton profile parameter $J(q)$ [9].

From the loss function, the real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric function can be calculated via the Kramers-Kronig transformation (KKT) [14]. Fig. 3 shows the ϵ_1 and ϵ_2 spectra of liquid benzene near the $\pi - \pi^*$ excitation energy. With increasing q , the $\pi - \pi^*$ band in ϵ_2 weakens, in line with the decrease in the corresponding band in $\text{Im}(-1/\epsilon)$. In contrast to the systematic dispersion in $\text{Im}(-1/\epsilon)$ (see Fig.1 (a): $\propto q^2 \times \text{Im}(-1/\epsilon)$), no marked peak dispersion is found for ϵ_2 . On the other hand, the amplitude of the variation in ϵ_1 is reduced significantly as q increases.

From the ϵ_2 spectra, it is clear that the $\pi - \pi^*$ band is narrow and almost flat, indicating that the transition in the liquid is well localized. This is consistent with the similarity of IXS spectra in Figs.1 (a)-(d). The peak width is possibly not due to the band-formation in the liquid but to the lifetime of the excited state, which is suggested to be larger than 0.66 eV [15].

3-3 The negative dispersion in the loss function.

Since the ϵ_2 spectra show no marked dispersion in liquid benzene, the negative dispersion of the $\pi - \pi^*$ band in the loss function, $\text{Im}(-1/\epsilon) = \epsilon_2 / (\epsilon_1^2 + \epsilon_2^2)$, must be attributed to variations of the denominator with q . The denominator represents the degree of shielding of the interactions, and was called 'a shielding factor' by Inokuti [1]. The effect of the shielding factor on the peak energy E_{peak} in $\text{Im}(-1/\epsilon)$ can be clearly illustrated by using the well-known Lorentz model [16], where E_{peak} for a single band located at E_b in ϵ_2 is expressed as follows [17,18]:

$$E_{\text{peak}} \approx (E_b^2 + 4\pi\hbar^2 e^2 Nf / m)^{1/2} = (E_b^2 + fE_p^2)^{1/2}. \quad (1)$$

Here N is the number density of electrons relating to the excitation, f is the oscillator strength describing the band intensity in ε_2 , and m and e are the electronic mass and charge. The second term in eq. (1) includes a square of plasma energy E_p [3,14] and reflects the shielding effect. Whereas the first term in eq. (1) dominates in gases ($N \sim 0$) and the second dominates in metals ($E_b \sim 0$), both terms contribute to E_{peak} in molecular liquids because $N > 0$ and $E_b \geq fE_p$. Hence, the negative q -dispersion of E_{peak} can be interpreted using eq. (1), since f is large at $q \sim 0$ and decreases with q as has been shown in Fig. 3.

The smaller dispersion in the benzene-hexane solutions can be also explained by the above mechanism. When the band intensity decreases by dilution, which is equivalent to reducing N in eq. (1), the shift of E_{peak} by the shielding effect decreases also. Indeed, for the 25 mol% solution, the energy difference ($E_{\text{peak}} - E_b$) at $q=0$ can be estimated to be ~ 0.054 eV¹, which is too small to be observed by the present experimental resolution (0.5 eV).

3-4. The loss function on molecules in condensed phases

The present study indicates that the $\pi - \pi^*$ excitation in the liquids studied is localized at each benzene ring, and can be well described by the independent oscillator model (Lorentz model). Similar results can be expected for discrete excitations in most molecular liquids and solids, where intermolecular interaction is as weak as that in benzene. Thus, it can be meaningful to analyze or estimate the loss function, $\text{Im}(-1/\varepsilon(q, E))$, of discrete excitations in condensed phases by employing data of isolated molecules, which can be measured by inelastic scattering of gases [12,13] or can be calculated by using the molecular orbital method [19]. However, the shielding effect has to be considered, especially for strong bands, as has been shown by this work. Therefore, the experimental deduction of not only $\text{Im}(-1/\varepsilon(q, E))$ but also $\varepsilon_1(q, E)$ and $\varepsilon_2(q, E)$ on target molecular condensates is indispensable, although the measurements are time consuming because the $\text{Im}(-1/\varepsilon)$ spectra over a wide E range are needed to perform KKT.

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Footnotes

¹ By employing the values for E_b^2 of diluted benzene (45.02 eV²) and the fE_p^2 of pure benzene (2.92 eV²) in ref.15, the $E_{\text{peak}} - E_b$ value at $q=0$ for the 25 mol% solution can be estimated to be $(45.02 + 0.25 \times 2.92)^{1/2} - (45.02)^{1/2} \approx 0.054$ eV.

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Figure captions

Fig.1 The q -dependence of the $\pi - \pi^*$ band in IXS spectra of liquid benzene (a), liquid toluene (b), solid polystyrene (c), and 25 mol% benzene-hexane solution (d).

Fig.2 The loss function of liquid benzene.

Fig.3 The real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric function of liquid benzene.

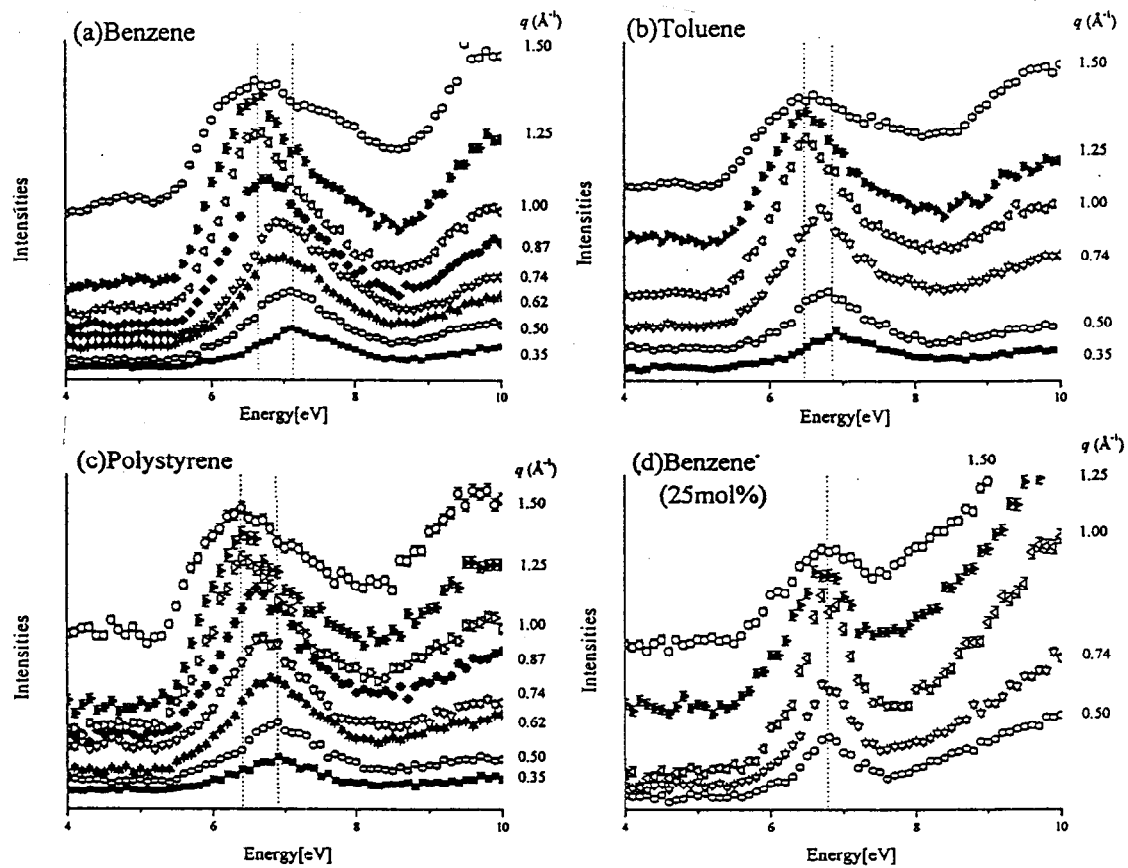


Fig.1

Hayashi et al,

Momentum dependence of $\pi - \pi^*$ excitations of benzene rings in condensed phases

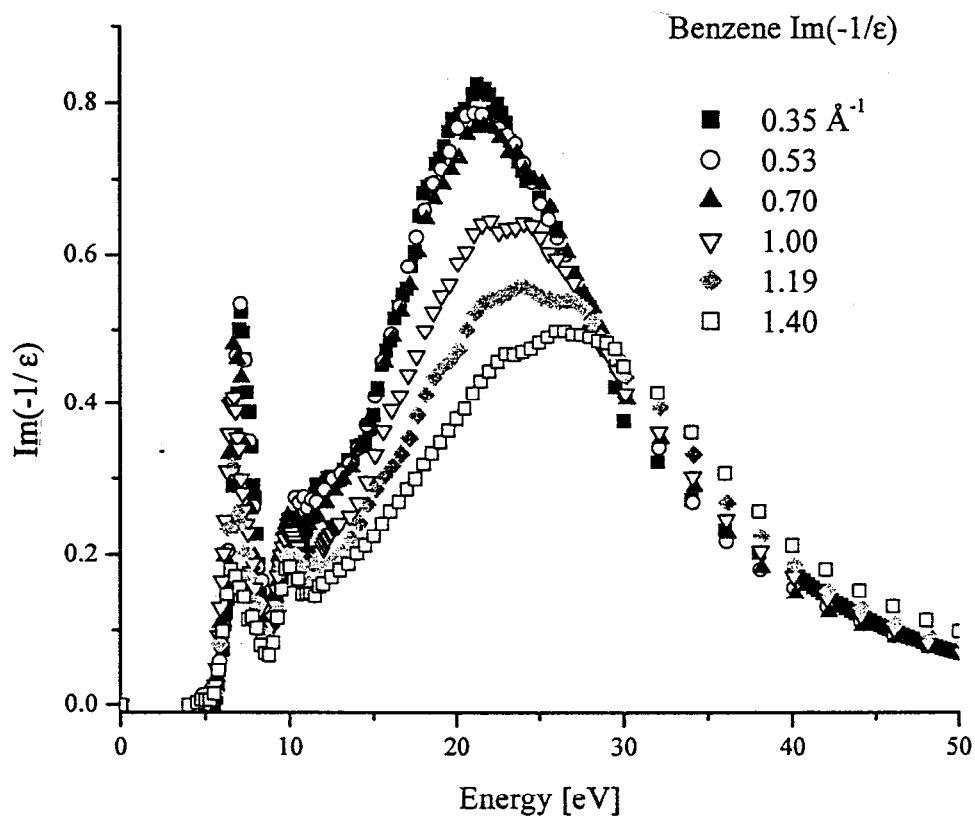


Fig.2

Hayashi et al,

Momentum dependence of $\pi - \pi^*$ excitations of benzene rings in condensed phases

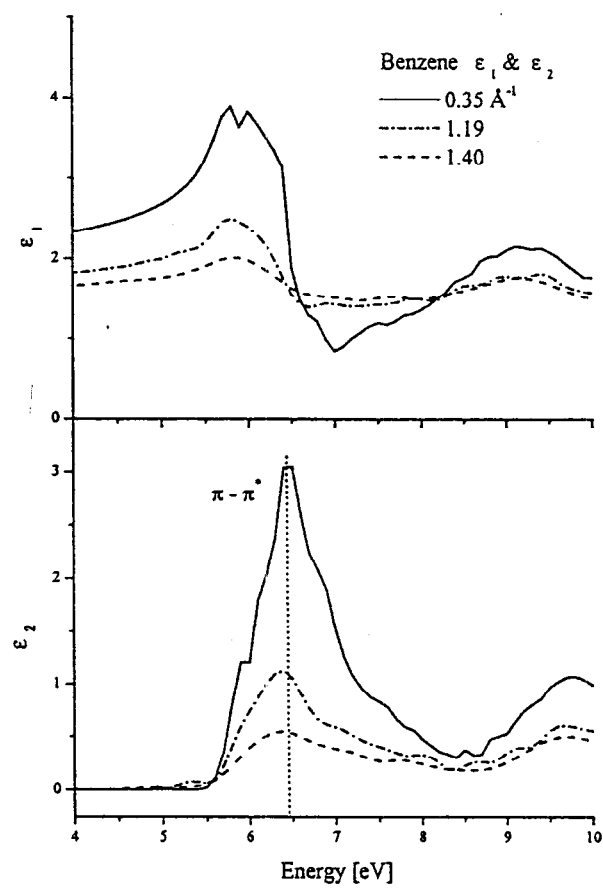


Fig.3

Hayashi et al,

Momentum dependence of $\pi - \pi^*$ excitations of benzene rings in condensed phases

